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Short communication

Effect of $Fe(CN)_6^{3-}$ | ITO interfacial cathodic current on the efficiency of the photoelectrochemical *n*-PbO | $Fe(CN)_6^{3-/4-}$ | ITO cell

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1. Introduction

In a photoelectrochemical (PEC) cell, photopotential depends mainly on the nature of the junction at the semiconductor–electrolyte interface. Photocurrent depends, apart from other factors, on the magnitude and reversibility of the cathodic current at the counter electrode [1]. Although platinum is the most ideal inert electrode, it is costly and its opaque nature limits use as counter electrode. An opaque electrode can only be used by placing it behind a semiconductor electrode, which hinders mass transfer of electrolyte from the semiconductor to the counter electrode and vice versa. A transparent counter electrode like indium tin oxide (ITO) seems to be the next best choice as a counter electrode [1]. This invites a study to confirm whether the cathodic reaction occurring at the ITO glass electrode with $Fe(CN)_6^{3-/4-}$ in a PEC cell: α-PbO| $Fe(CN)_6^{3-/4-}$ | ITO [2–5] is as reversible as the platinum counter electrode. This paper describes such a study.

2. Experimental details

n-type α-PbO thin films were potentiodynamically synthesized from pure lead, in the potential range -0.2 V to $+0.2$ V (Hg/HgO) in alkaline medium as described elsewhere [5]. All potentials were measured with respect to a Hg/HgO electrode, unless specified otherwise. The surface of a highly conducting (10 $\Omega/\square$) transparent indium tin oxide (ITO) sheet was modified with platinum. This was achieved by depositing platinum potentiodynamically (-0.5 to $+0.5$ V vs SCE) over the ITO sheet in a single sweep (100 mV s^{-1}) from a solution of 10^{-2} M H_2PtCl_6 (pH 2) (Figure 1(a)). Transparency of the ITO sheet was not affected by deposition of a small amount of platinum. This ITO sheet hereafter is referred to as the modified ITO electrode. Photoelectrochemical measurements were carried out using a stabilized 100 W tungsten–halogen lamp in conjunction with a microprocessor controlled monochromator (Acton Research Corporation, model 150), Lock-in analyser (PAR, model 5204), potentiostat/galvanostat (Pine, model AFRDE4) and a chopper (Par, model 197). Photocurrents during white light illumination were digitally recorded by a Keithley Metrabyte DAS-1601 I/O board. Stability studies of the PEC cell were carried out using a potentiostat (EG&G, model Versastat) connected to a PC.

3. Results and discussion

The cathodic I/V curves of 0.1 M $Fe(CN)_6^{4-}$ + 0.01 M $Fe(CN)_6^{3-}$ (pH 9.2), at the ITO sheet (Figure 1(a)), the platinum (Figure 1(c)) and surface modified ITO glass (Figure 1(d)) show that not only the cathodic current at the ITO sheet is small, but the change in current/voltage (i.e., the slope of the cathodic current) is also smaller than observed with platinum, suggesting slow charge transfer kinetics at the ITO electrode. After modification of the ITO electrode surface, the cathodic slope of the I/V curve (Figure 1(d)) shifted nearer to the slope given by platinum (Figure 1(b)), which suggest an improvement in the kinetics of charge transfer at the modified ITO electrode surface. Tenne et al. [1] have also observed a similar improvement with CdS (using modified ITO glass as a counter electrode).

The effect of variation in cathodic current (biased) on the efficiency of the PEC cell was analysed from the current–voltage characteristics. First, an I/V curve of α-PbO | 0.1 M $Fe(CN)_6^{4-/3-}$| was obtained in darkness (Figure 2(a)). Then the configuration was illuminated

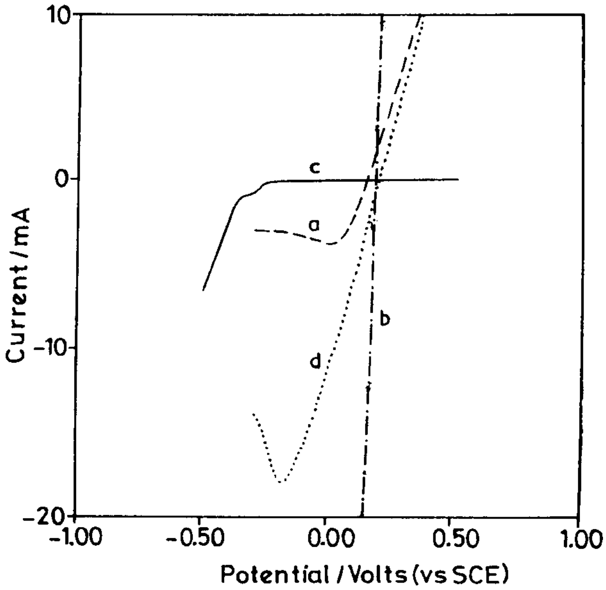

Fig. 1. (c) Cathodic half cycle plot of ITO electrode in 10^{-2} M H_2PtCl_6 solution (i.e., for surface modification of ITO electrode with platinum). I/V curve in 0.1 M $Fe(CN)_6^{4-}$, 0.01 M $Fe(CN)_6^{3-}$ solution with (a) ITO electrode, (b) Pt electrode, (d) surface modified ITO electrode with platinum.

with white light of 100 mW cm^{-2} and the corresponding I/V curve taken (Figure 2(b)). Finally, the I/V curve of bare ITO in 0.1 M $Fe(CN)_6^{4-}$ +0.01 M $Fe(CN)_6^{3-}$ was obtained (Figure 2(c)). These three plots were superimposed (Figure 2) to analyse cell efficiency. This superimposition of three curves gives an idealized current–voltage curve of the PEC cell. If the ITO electrode had behaved fully reversibly, the maximum short-circuit current should have been y instead of y_o (Figure 2). In other words, due to the poor response of the ITO

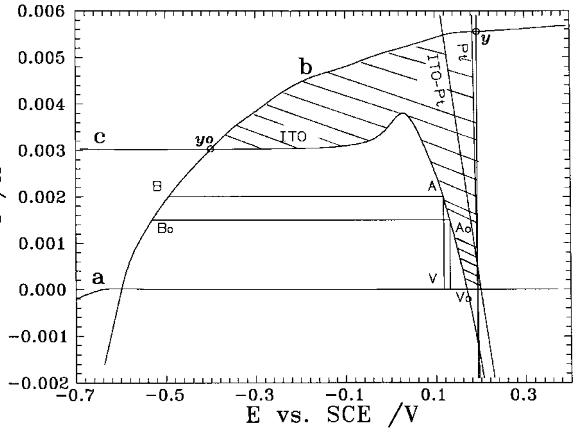

Fig. 2. I/V curve of α-PbO | 0.1 M $Fe(CN)_6^{4-}$, 0.01 M $Fe(CN)_6^{3-}$|: (a) In dark, (b) under white light illumination. Curve (c) is the I/V curve of the ITO in 0.1 M $Fe(CN)_6^{4-}$, 0.01 M $Fe(CN)_6^{3-}$ solution (Figure 1(a)).

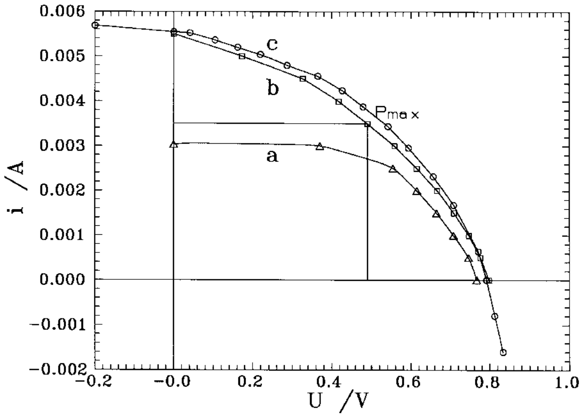

Fig. 3. Power curve of α-PbO photoanode of the PEC cell using different counter electrodes (a) ITO, (b) surface modified ITO with platinum, (c) platinum electrode.

electrode, the electrical power which should have been available by the PEC cell is lost to the extent shown by the shaded area of the curve.

The power characteristics of the cell were generated (Figure 3) after considering the influence of the counter electrode on the PEC cell (Figure 2). For this purpose, at periodic intervals, horizontal lines (AB, A_0B_0 etc.) were drawn (Figure 2). The lengths of these horizontal lines correspond to the magnitudes of the corresponding photopotential. The corresponding photocurrent was calculated by drawing vertical parallel lines AV, A_0V_0 etc. Thus, for photopotentials of magnitude AB, A_0B_0, the corresponding photocurrents are AV and A_0V_0, respectively. A series of data was generated in this fashion, and photopotentials and corresponding photocurrents were plotted to obtain the power curve for the PEC cell (Figure 3(a)) operating with the ITO sheet as a counter electrode. From this graph, the power conversion efficiency (η) and the fill factor (ff) were calculated. Similar exercises were done to study the influence of platinum coated ITO (Figure 3(b)) and pure platinum (Figure 3(c)) as counter electrodes in this PEC cell. The results are listed in Table 1. Figure 3 and the results given in Table 1 suggest that, although the photopotential is similar for all these three systems, the short circuit currents are different and the efficiency of the cell is least

Table 1. Comparison of efficiencies of the PEC cell using different counter electrodes

Counter electrode	I_{sc} /mA cm^{-2}	V_{oc} /mV	η /%	ff
Pt	5.54	792	1.86	0.42
ITO(Pt)	5.50	798	1.73	0.39
ITO	3.03	767	1.38	0.59

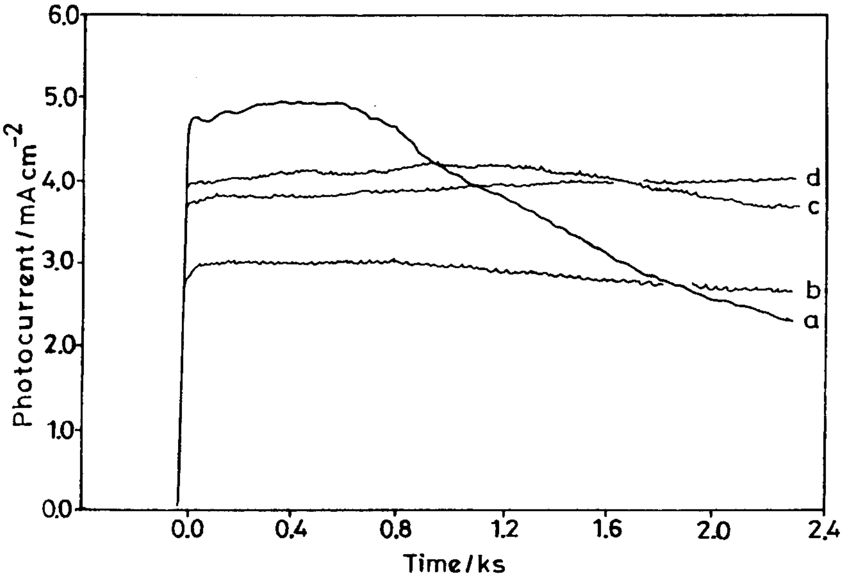

Fig. 4. I/t behaviour of α-PbO photoanode in the PEC cell using different counter electrodes (a) Pt, (b) ITO, (c) Pt coated ITO and (d) modification of plot (c) after adding CsI to the electrolyte.

for the ITO glass. However, the efficiency of photoconversion to electrical power is improved considerably by surface modification of the ITO glass electrode.

Our next approach using another PbO electrode was to study the influence of the counter electrode (i.e., Pt, ITO sheet and modified ITO glass sheet) on the stability of this PEC cell. α-PbO was illuminated with a white light of 100 mW cm^{-2} and the short-circuit photocurrent was measured for various illumination times (Figure 4). As expected, the magnitude of the initial photocurrent was highest with pure platinum (Figure 4(a)) and least with ITO (Figure 4(b)). But the magnitude of the photocurrent was found to be almost constant over a period of 2400 s of continuous illumination with the modified ITO electrode (Figure 4(c)) as compared to the platinum electrode. CsI (Figure 4d) seems to have a stabilizing effect. On this we shall report in a separate paper.

4. Conclusion

This study suggests that the cathodic current at the counter electrode in a α-PbO | $Fe(CN)_6^{3-/4-}$ PEC cell affects the efficiency considerably and, hence, it is essential to develop a counter electrode which gives a highly reversible cathodic current with the redox electrolyte used. The surface modified ITO counter electrode also shows a marked effect on the stability of the photoanode.

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